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## EUROPEAN PATENT APPLICATION

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⑤④ **Conductive thermoplastic compositions.**

⑤⑦ Thermoplastic compositions comprising a polycarbonate resin, an ABS-graft copolymer and aluminium flakes are provided suitable for the preparation of molded articles characterised in that they provide an improved level of EMI shielding.

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CONDUCTIVE THERMOPLASTIC COMPOSITIONS

SUMMARY OF THE INVENTION

Thermoplastic compositions comprising a polycarbonate resin, an ABS-graft copolymer and aluminium flakes are provided suitable for the preparation of molded articles characterised in that they provide an improved level of EMI shielding.

BACKGROUND OF THE INVENTION

Compositions comprising blends of a polycarbonate resin and an ABS resin were disclosed in U.S. Patents 3,130,177 and 3,852,393. The usefulness of these compositions has sometimes been limited due in part to the fact that they, like other polymeric compositions, are not protective in respect to electro-magnetic interference (EMI). EMI is caused by electromagnetic radiation from electronic and electric devices and disrupts the operation of business equipment and instrumentation generally. The use of plastics in fabricating enclosures for such equipment and instrumentations is quite wide spread primarily because of the cost advantage they present in comparison to other materials. Plastics, however, are transparent to EMI except where conductive materials have been incorporated therewith. The art is noted to include reports where conductive particles of the type used in the present invention have successfully been introduced in polycarbonates and in polyester resins in amounts of up to 20% by weight. (see sales brochure by the Trivalent Materials Group, Scientific Advances, Inc., a subsidiary of Battelle Memorial Institute of Columbus, Ohio)

Graft Copolymers

In the context of the present practice, graft copolymers are ABS (acrylonitrile-butadiene-styrene) resins

prepared by either bulk or bulk suspension polymerisation as distinguished from similar resins prepared by emulsion polymerisation. In terms of particle size distribution, the suitable ABS resins of the invention range from about 0.2 to about 10 microns preferably 0.2 to about 5 microns.

Essentially, the molecules of ABS graft polymers consist of two or more polymeric parts of different compositions chemically united. The graft polymers may be prepared by polymerising at least one conjugated diene, such as butadiene or a conjugated diene with a monomer polymerisable therewith, such as styrene or acrylonitrile, to provide a backbone, with subsequent polymerisation of grafting monomers, in the presence of the prepolymerised backbone to complete the graft polymer.

The grafting monomers consist at least of one monovinyl aromatic hydrocarbon and at least of one ethylenically unsaturated nitrile.

The backbone, as mentioned, is preferably a conjugated diene polymer or copolymer such as polybutadiene, butadiene-styrene, butadiene-acrylonitrile, polyisoprene or the like.

The preferred conjugated diene utilised herein is butadiene.

The monovinyl aromatic monomers utilised are selected from the group consisting of 3-methylstyrene; 3,5-diethylstyrene and 4-n-propylstyrene, *o*-methylstyrene, *o*-methylvinyltoluene, *o*-chlorostyrene, vinyltoluene and *o*-bromostyrene.

The preferred monovinyl aromatic hydrocarbon used herein is styrene and/or *o*-methylstyrene.

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The second group of monomers that are polymerised in the presence of the prepolymerised backbone are acrylonitrile, methacrylonitrile,  $\alpha$ -chloroacrylonitrile or  $\alpha$ -bromoacrylonitrile. Preferred is acrylonitrile. Preferred mixtures of grafting monomers are mixtures of acrylonitrile with styrene or with  $\alpha$ -methylstyrene in combination with up to 20wt% styrene.

In the preparation of the graft polymer, the conjugated diolefin polymer or copolymer exemplified by 1,3-butadiene polymer or copolymer comprises from about 60% by weight to about 5% by weight, preferably from 8 to 20% by weight of the total graft polymer composition, and the monomers polymerised in the presence of the backbone exemplified by styrene and acrylonitrile comprise from about 40 to about 95% by weight, preferably from 80 to 92% by weight, of the total graft polymer composition.

The second group of grafting monomers, the ethylene ~~ally~~ unsaturated nitriles of the graft polymer composition, preferably comprise from about 10% to about 40% by weight of the total graft copolymer composition and the monovinyl aromatic hydrocarbons, preferably comprises from about 30 to about 70% by weight of the total graft polymer composition.

In preparing the graft polymer of this invention, a certain percentage of the polymerising monomers that are grafted on the backbone will occur as free copolymer. If styrene is utilised as one of the grafting monomers and acrylonitrile as the second grafting monomer, a certain portion of the composition will occur as non-grafted styrene acrylonitrile copolymer. In certain instances, one of the first group, i.e., monovinyl aromatic monomers such as  $\alpha$ -methylstyrene is copolymerised with one of the second group, i.e., acrylonitrile, substituted acrylonitrile, etc., and a certain percentage of the composition is comprised of, for example, an  $\alpha$ -methylstyrene acrylonitrile copolymer.

It is contemplated in this invention that the composition referred to as graft polymer contain up to 80% copolymer existing either as free copolymer from preparation of the graft or as an added copolymer component. These added copolymers are preferably materials having high heat distortion temperatures such as is the case when  $\alpha$ -methylstyrene acrylonitrile copolymers are added.

Essentially, the ABS resins of the invention prepared by bulk-suspension polymerisation are described more fully in U.S. Patent 3,852,393, especially column 6, line 30. The bulk polymerisation is e.g. described in German Offenlegungsschriften No. 30 47 293 and No. 17 70 392. Compare also Br. Polymer J. 1974, pages 205 to 228. The bulk-suspension process proceeds as follows: Dissolving a butadiene type rubber, such as polybutadiene or a butadiene styrene copolymer, in a mixture of vinyl cyano compound represented, for example, by acrylonitrile, and a vinyl aromatic hydrocarbon represented by styrene, polymerising the mixture substantially under bulk polymerisation conditions, under sufficiently high agitation so as to shear the rubber being precipitated as polymerisation advances until 10 to 40% by weight of the vinyl cyano compound and vinyl aromatic compound are polymerised, and then adding water and a suspension stabiliser to the polymerisation system and continuing the polymerisation under the suspension polymerisation conditions until the polymerisation is substantially completed. The resulting ABS contains crosslinked rubber particles of 0.2 to 10 microns.

The known bulk polymerisation proceeds as follows: After dissolving the butadiene rubber in the monomer mixture, optionally by adding some solvent, radical polymerisation starts and will be continued under stirring up to a percentage of 10 to 40 wt% of polymerised mono-

mers, referred to the total weight of polymerisable monomers. After obtaining the so called "phase inversion" polymerisation is continued by grafting and cross-linking the rubber up to an amount of 40 to 95 wt% of polymerisation of the monomers, referred to the total weight of polymerisable monomers. The resulting ABS contains crosslinked rubber particles of 0.2 to 10 microns.

Instant preferred ABS compositions are those obtained by bulk polymerisation.

In the preferred practice, butadiene-styrene copolymers prepared by the solution polymerisation process using an organic metal compound as catalyst is used as the butadiene type rubber. Specifically, rubbers prepared by solution polymerisation yield products having better properties (better transparency, less coloration) than rubbers of the emulsion polymerisation type.

#### The Polycarbonate Resin

The polycarbonate resins useful in the practice of the invention are homopolycarbonates, copolycarbonates and terpolycarbonates or mixtures thereof. The polycarbonates generally have molecular weights of 10,000-200,000 (average molecular weight), preferably 20,000-80,000 and may have a melt flow rate per ASTM D-1238 at 300°C of about 1 to about 24 gm/10 min., preferably about 2-6 gm/10 min. They may be prepared, for example, by the known diphasic interface process from phosgene and bisphenols by polycondensation (see the monograph, H. Schnell, "Chemistry and Physics of Polycarbonates", Interscience Publisher, New York, 1964, incorporated herein by reference).

Among the useful bisphenols in the practice of the invention are hydroquinone, resorcinol, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfoxides, bis-(hydroxyphenyl)-sulfones and  $\alpha,\alpha$ -bis-(hydroxyphenyl)-diisopropyl-benzenes,

as well as their nuclear-alkylated compounds.

Further suitable aromatic dihydroxy compounds are described, for example, in U.S. Patents 3,028,365; 2,999,835 and 2,999,846. Further examples of suitable  
5 bisphenols are 2,2-bis-(4-hydroxy-phenyl)-propane (bisphenol A), 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane,  $\alpha,\alpha$ -bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-methyl-4-hydroxy-phenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-  
10 propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfoxide, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, hydroxybenzophenone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)-cyclohexane,  $\alpha,\alpha$ -bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene, 4,4'-sulfonyl diphenol.

Examples of particularly preferred aromatic bisphenols are 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

The most preferred bisphenol is 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A).

The polycarbonates of the invention may entail in their structure units derived from one or more of the suitable bisphenols.

Among the resins suitable in the practice of the invention are included phenolphthalein-based polycarbonate copolycarbonates and terpolycarbonates such as are described in U.S. Patents 3,036,036 and 4,210,741.

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The polycarbonates of the invention may also be branched by incorporating small quantities of polyfunctional (preferably polyhydroxy) compounds in them by condensation, e.g., 0.05 - 2.0 mol % (based on the quantity of bisphenols used). Polycarbonates of this type have been described, for example, in German Offenlegungsschrift 1,570,533; British Patent 1,079,821 and US Patent 3,544,514. The following are some examples of polyhydroxyl compounds which may be used for this purpose: phloroglucinol; 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptene-2; 1,3,5-tri-(4-hydroxyphenyl)-benzene; 1,1,1-tri-(4-hydroxyphenyl)-benzene; 2,2-bis-[4,4'-(4,4'-dihydroxydiphenyl)-cyclohexyl]-propane; 2,4-bis-(4-hydroxyphenyl-4-isopropyl)-phenol; 2,6-bis-(2'-dihydroxy-5'-methylbenzyl)-4-methylphenol; 2,4-dihydroxybenzoic acid; 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane and 1,4-bis-(4',4''-dihydroxytriphenylmethyl)-benzene. Among the other useful polyfunctional compounds are 2,4-dihydroxybenzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

In addition to the polycondensation process mentioned above and which essentials are described below, other processes for the preparation of the polycarbonates of the invention are polycondensation in a homogeneous phase and transesterification.

The preferred process for the preparation of polycarbonates is the interfacial polycondensation process.

Other methods of synthesis in forming the polycarbonates of the invention such as disclosed in U.S. Patent 3,912,688 may be used.

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### Conductive Particles

The conductive particles suitable in the context of the present invention are aluminium flakes characterized in that their resistivity (in micro-ohms-centimeter at 20°C) is below 15, preferably below 10 and in that their largest dimension does not exceed 0.250". Preferably, the flake thickness may average from about 0.0008" to about 0.10", preferably about 0.001" to about 0.005" and while their planar shape is not critical in the present context--square, circular, regular and irregular shapes are all possible--their projected area is preferably between about  $9 \times 10^{-4}$  and  $4 \times 10^{-3}$  inch<sup>2</sup>, preferably between  $16 \times 10^{-4}$  and  $25 \times 10^{-4}$  inch<sup>2</sup>. Aluminium flakes measuring about 0.040 x 0.050 x 0.001" are the preferred configuration. Aluminum flakes suitable for the purpose are available commercially under the trade name Transmet<sup>®</sup>, from Scientific Advances, Inc., a subsidiary of Battelle Memorial Institute of Columbus, Ohio.

The compounding of the compositions in accordance with the present invention was carried out using a twin screw, intermeshing co-rotating extruder ZSK 53V by Werner Pfleider, screw rpm 105, at a temperature profile as shown in Figure 1. Certain practices and modifications as described herein below were found to be necessary in order to obtain a homogeneous mixture of resin and aluminum flakes with minimum flake deformation. Since aluminum flakes are characterized both by their low bulk density and by their high thermal conductivity, they tend to float on

the surface of the molten resin and cause rapid local freezing of the melt. In order to alleviate the problem, it was found that the flakes best be accurately metered into the homogeneous melt downstream from a high intensity mixing zone. Further, it was found that the flow of the flakes needs to be directed to the area of the screw set which is turning into the extruder body, axial to the screw. The flakes also were directed so as to impinge on only 1 to 1½ flights of the exposed screw as they advanced to re-enter the extruder body. Control of the transverse and axial directions of the flow of the flakes results in that all of the flakes entry was confined to an area within one turn of the screw and was accomplished by using a hopper having a 60° inclined plane positioned parallel to the direction of extrusion (see Figure 2). In order to eliminate the flotation action of rising volatiles and heated air counter-current to the descending flakes, a slight vacuum was drawn on the space above the exposed screw. It was further found that entry of the flakes into the melt is best carried out at more than one location as shown in Figure 1. Downstream of the first location of the entry of the flakes, the polymer/flakes mixture was subjected to a medium intensity distributive mixing zone so as to present a homogeneous mixture at the subsequent point of entry of the flakes. Downstream of that subsequent entry point, low intensity mixers were used to avoid, or at least minimize, deformation of the flakes while providing the necessary pressure to form the melt into strands by forcing it through the die. The strands were then cooled and chopped into pellets useful for

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injection molding or other thermoplastic forming processes.

Figure 1 is a schematic representation of the extrusion process--side view--indicating the temperature profile, the corresponding mixing zones and the points of entry of the aluminum flakes into the molten resin.

In Figure 1, is the location of entry of the polycarbonate/graft polymer mixture. 2 and 3 are locations of entry of the conductive particles. The mixing sections along the extruder barrel are numbered 4, 5 and 6 in the figure and denote a medium, high and low intensity mixing section, respectively.

Figure 2 is a schematic representation of a cross-section of the extruder at the point of entry of the conductive particles. A is a hopper positioned over a screw B and C is a vacuum vent as described above.

In the practice of the invention compositions comprising the resin blend and conductive particles may be prepared as described above. The resin blend may be characterized in that the weight ratio between the polycarbonate resin and the graft copolymer is between about 30/70 and about 70/30, more preferably between about 40/60 and about 60/40. The compositions of the invention may be further characterized in that the amount by volume of the conductive particles may be between about 8%, to about 25%, more preferably between about 12 to about 20%, most preferably between about 14 and 18%, all percents being relative to the volume of the blend plus that of the conductive particles.

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# EXAMPLES

Tables 1 and 2 summarize the properties of the compositions of the invention set in comparison to a control wherein ABS was of the emulsion polymerization type. In the Examples the compositions all contain 40% by weight aluminum flakes (about 14.8 volume %) and the polycarbonate resin was Merlon<sup>®</sup> M-50, a bisphenol-A-polycarbonate of Mobay Chemical Corporation, having a melt index per ASTM D-1238 of about 3 - 5.9 gm/10 min. The graft copolymer was Dow<sup>®</sup> 213, an ABS resin prepared by bulk polymerisation, and available from Dow Chemical

Corporation and the conductive particles were aluminum flakes available commercially as Transmet K-162<sup>®</sup> and K-102HE from Scientific Advances, Inc., Columbus, Ohio. Coupling agents as known in the art, such as silanes and/or titanates, may be successfully used in the context of the invention as is demonstrated by the use of K-162<sup>®</sup> (composition II). The ABS resin used, termed Dow<sup>®</sup> 213, is characterized in that its particle size ranges from about 0.2 to about 2.5 micron with an average at nearly 1 micron and in that about 75% of the particles are smaller than 1 micron and in that its acrylonitrile content is about 14%, its butadiene content is about 8-10% the balance being styrene, and further in that its specific gravity is 1.05. Other properties characterizing Dow<sup>®</sup> 213 are listed below

Rockwell hardness, R scale	110
Izod impact, notched ft.lb/in 1/8"	2.9
1/4"	2.1
Heat distortion temp. at 264 psi, °C	78
Tensile yield, psi	5100
Tensile ultimate strength, psi	4800
Elongation, % yield,	5

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ultimate	5.5
Flexural strength, psi	8400
Flexural modulus, psi x 10 <sup>-5</sup>	3.4

In the Examples, the ratio of polycarbonate to 5 the ABS was 55/45% by weight.

As is clearly demonstrated by the results of Tables 1 and 2, the compositions in accordance with the practice of the invention combine good mechanical properties, effective EMI shielding and good process-  
10 ability. The advantages of these compositions over their counterparts where ABS resins prepared by the emulsion polymerization are clearly evident upon the comparative values of spiral flow and EMI shielding.

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TABLE 1

	Control (1)	I (2)		II (3)	
		500°F	525°F	500°F	525°F
Melt temperature					
Tensile strength, psi x 10 <sup>3</sup>	4.30	4.00	4.64	4.40	4.54
Flexural strength, psi x 10 <sup>3</sup>	8.60	9.86	10.30	10.15	10.15
Flexural modulus, psi x 10 <sup>5</sup>	3.70	7.61	8.30	7.85	7.77
Impact strength, notched					
Izod, ft.lb/in. 1/8"	1.8	1.9	2.0	1.9	1.8
1/4"	2.0	1.9	1.8	1.9	1.8
Unnotched, ft./lb/in.					
1/8"	3.1	3.0	2.7	2.9	2.7
1/4"	4.0	2.6	3.2	2.8	2.9
Compression strength psi x 10 <sup>3</sup>		12.4	-	12.7	-
Hardness, M scale		60	-	56	-
Heat deflection temperature, °F at 264 psi	235	222.8	225.0	223	221
at 66 psi	225	233.6	230.0	232	235
Vicat softening temp. (B), °F		280	-	277	-
dc Resistivity, ohm-cm	0.5	0.000	-	0.000	-
Spiral flow (0.100 wall thickness), inches	8	12	14	13	15

(1) the composition based on emulsion polymerisation ABS, having the same content of acrylonitrile, butadiene and styrene as DOW<sup>®</sup> 213.

(2) aluminium flakes K-102HE<sup>®</sup>

(3) aluminium flakes K-162<sup>®</sup>

TABLE 2

Frequency MHz	Shielding (Transmission line) Attenuation (dB)		
	Control (1)	I (2)	II (3)
0.5	40	63	56
1.5	41	63	55
5	41	63	54
15	40	60	54
50	40	59	54
250	36	48	41
500	—	45	40
960	—	42	39

(1) the composition based on emulsion polymerisation ABS, having the same content of acrylonitrile, butadiene and styrene as DOW<sup>®</sup> 213.

(2) aluminium flades K-102HE<sup>®</sup>

(3) aluminium flakes K-162<sup>®</sup>

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WHAT IS CLAIMED IS:

1. A thermoplastic molding composition comprising aluminium flakes, a resinous blend of a polycarbonate resin and an ABS graft polymer prepared by either bulk or bulk suspension polymerization.
2. The composition of Claim 1 wherein the amount of said polycarbonate relates to that of said graft copolymer as from about 30/70 to 70/30.
3. The composition of Claim 1 wherein said aluminium flakes are present in an amount of between about 8 to about 25% relative to the total volume of said blend and said aluminium flakes.
4. The composition of Claim 1 wherein said flakes are treated with a coupling agent.

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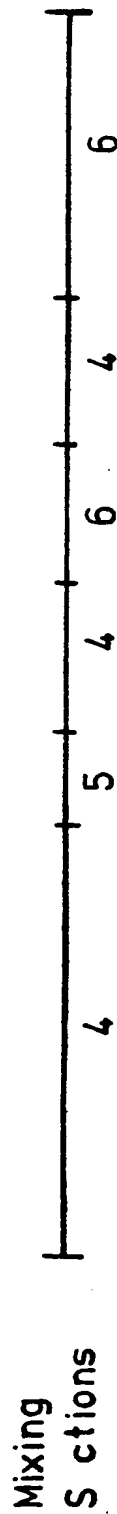
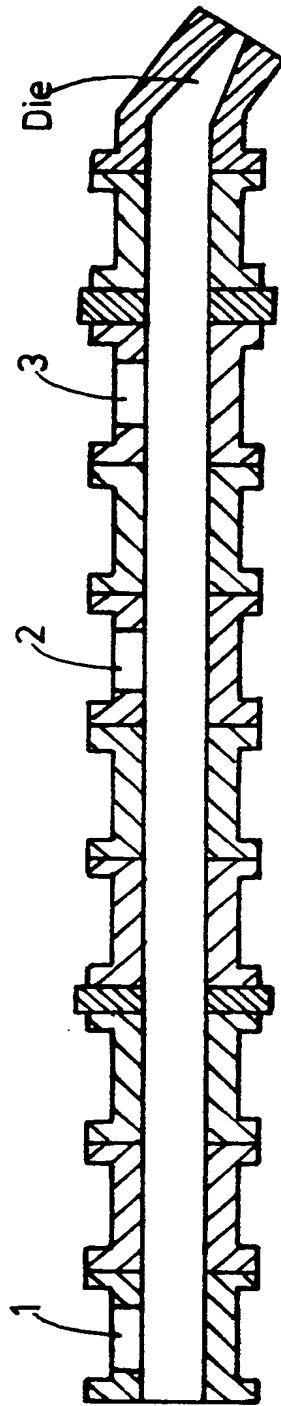
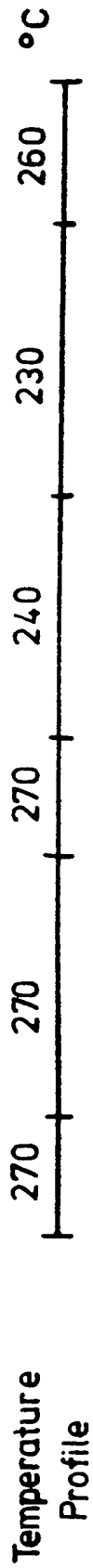


FIG.1

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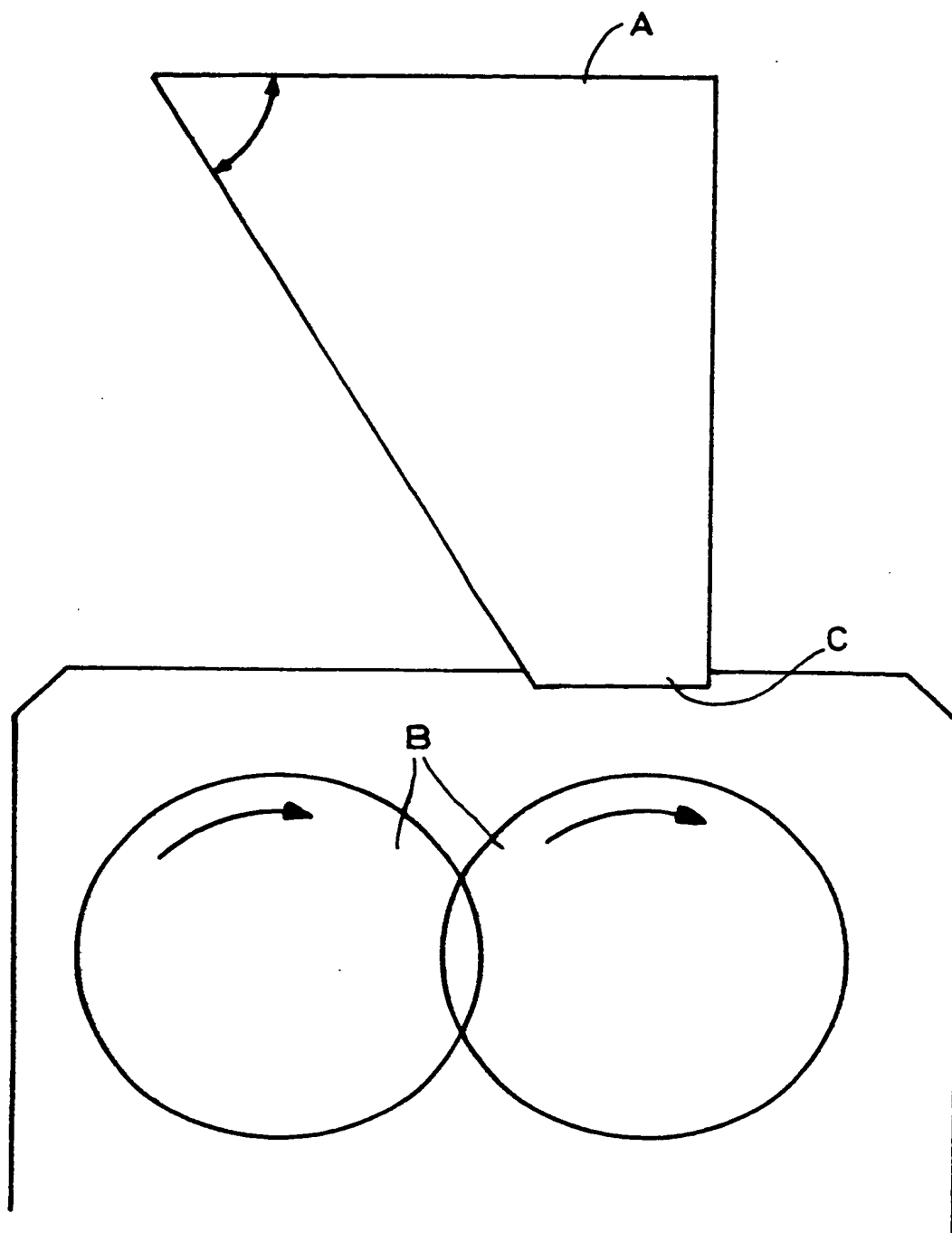


FIG. 2



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# EUROPEAN SEARCH REPORT

0107015 Application number

EP 83 10 9102

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. <sup>3</sup> )
D, A	US-A-3 130 177 (T. S. GRABOWSKI)		H 01 B 1/22 C 08 L 69/00
D, A	US-A-3 852 393 (S. FURUKAWA)		
A	US-A-3 654 187 (H. TAKENAKA)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. <sup>3</sup> )
			H 01 B 1/00 C 08 L 69/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20-01-1984	Examiner STIENON P.M.E.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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